Corrosion Aspects of High-level Waste Disposal in Salt Domes

Rørbo, K.

Publication date:
1979

Document Version
Publisher's PDF, also known as Version of record

RISØ

Metallurgy Department

S-7913

Risø-I-63

December 1979

CORROSION ASPECTS OF HIGH-LEVEL WASTE DISPOSAL IN SALT DOMES

K. RØRBO

This report has been worked out according to the agreement between Risø National Laboratory and ELSAM/ELKRAFT concerning advisory assistance from Risø to ELSAM/ELKRAFT's waste management project, phase 2.

RISØ

Metallurgy Department

December 1979

S-7913

Risø-I-63

CORROSION ASPECTS OF HIGH-LEVEL WASTE DISPOSAL IN SALT DOMES

K. RØRBO

This report has been worked out acccrding to the agreement between Risø National Laboratory and ELSAM/ELKRAFT concerning advisory assistance from Risø to ELSAM/ELKRAFT's waste management project, phase 2.

Risø - I - 63

Titel og forfatter(e)

CORROSION ASPECTS OF HIGH-LEVEL WASTE DISPOSAL IN SALT DOMES.

K. Rørbo

Dato December 1979

Afdeling eller gruppe

Metallurgi

Gruppens eget registreringsnummer

S-7913

19 sider + 12 tabeller + 10 figurer

Resumé

In the ELSAM/ELKRAFT waste management project it is planned that the high-level waste is glassified, encapsuled in canisters and finally deposited in a deep hole drilled in a salt dome. In the present report corrosion aspects of the canisters after deposition are discussed. The chemical environment will probably be a limited amount of brine coming from brine inclusions in the surrounding salt and moving up against the temperature gradient, the temperature at the canister surface being in the range of 100-150°C. The possible types of corrosion and the expected corrosion rates for a number of potential canister materials (mild steel, austenitic and ferritic stainless steels, Ni-base alloys, copper, titanium and a few combinations of materials) are discussed. Mild steel (possibly combined with an inner layer of copper or titanium) might possibly be an appropriate choice of material for the canister.

Kopier til:

Biblioteket (2)

Corrosion aspects of high-level waste disposal in salt domes.

Contents Page

Corrosion aspects of high-level waste disposal in salt domes.

1. Introduction

The two major Danish utility groups, Elkraft and Elsam, are carrying out a study of disposal of high-level radioactive waste in Denmark. The preliminary examinations (the phase 1 project) have confirmed that it is possible to build a repository in a suitable salt dome and that it is highly probable that a suitable salt dome can be found among the Danish domes in Jutland.

In the phase 2 project, running in the period 1979-80, more detailed investigations will be carried out, concentrating on layout and safety analysis of the repository and including geophysical measurements and test drillings in a few selected salt domes. It is the intention to carry the work far enough to make possible the provision of the documentation necessary for safe waste disposal.

In the project it is assumed that the high-level waste is glassified, encapsuled in some sort of canister and possibly in some further corrosion resistant overpack and finally deposited in holes drilled in the salt dome. The safety from release of radioactive isotopes to the environment (contamination of potable ground water layers etc.) is based primarily on the impermeability and geologic stability of the salt domes.

Potential release mechanisms have been discussed (ref. 1) and it is found that it is very difficult to imagine a situation resulting in an unacceptable release of radioactive isotopes to the water bearing surface layers. The most unpleasant situation mentioned in ref. 1 is flooding of the repository by water from the surrounding layers, penetrating into the closed salt dome due to a sudden disruptive event (earthquake, collapse along fracture zones, dissolution of unobserved Carnallite layers etc.) and taking place rather early after final disposal (e.g. after 100 years) and coinciding with the establishment of a drinking water well very close to the nuclide release point.

In order to minimize this already very small risk it is proposed to provide the waste cylinders with an overpack being sufficiently corrosion resistant and thereby for a long period

(hundreds or thousands of years) hindering the contact between the glass cylinder and the surrounding water.

Problems connected to the corrosion of possible overpack materials (corrosion rates, local corrosion, expected lifetime etc.) are discussed in the present report. The report is based on literature studies.

2. Environment

A detailed knowledge on how the corrosion environment around the waste cylinders will develop over a period of several hundred years will of course not be available. On the other hand a good deal of general information will still be present and some reasonable assumptions can be made on which considerations on the corrosion behaviour can be based.

2.1. Temperature

The relevant temperatures at the metal/salt interface will depend on the depth into which the disposal has taken place and on the rate of heat developed by the waste. It has been calculated (ref. 2), that the max. temperatures at the metal/salt interface at a depth of 3000 m will be approximately 150°C. This maximum temperature will be obtained 5 to 10 years after the disposal of the waste and will in the next few hundred years decrease towards approximately 100°C, which is the normal equilibrium temperature of the surroundings in that depth.

If a smaller depth is chosen for the disposal, the max. temperature will be correspondingly lower. At 500 m, e.g. the maximum temperature obtained will be approximately 75°C. It can be concluded that in consequence of these very limited temperatures dry oxidation will not play any role and that electrolytic corrosion will be the only significant type of corrosion.

The final choice of layout for the repository has not been made yet, and therefore the temperature of the surroundings is not known. For the present purpose (evaluation of corrosion problems) a temperature level in the range of 100° - 150°C at the metal surface is a reasonable assumption.

2.2. Brine

A necessary prerequisite for corrosion of the waste cylinders is that they come into contact with an aqueous solution. One possible source is the brine inclusions in the surrounding salt formations. It is well known that brine inclusions often are found in salt deposits, 0,5% being a typical amount. The diameter of the inclusions will typically be in the range of a few hundred /um. These inclusions will, supposing that they do not contain any gas or vapour, migrate through the salt upwards the temperature gradient, eventually resulting in a situation where the waste cylinder is surrounded by a layer of concentrated brine.

Until now no detailed information on the composition, pH, hydrolysis, radiolysis etc. of the brine is available. Under normal circumstances these factors would be of primary importance for the evaluation of the maximum corrosion rate. In the present case, however, the corrosion probably will be limited by another factor, viz. the amount of brine migrating to the cylinder. It has been calculated (ref. 3) that the accumulated brine inflow per meter of the cylinder is less than 0,5 l in 10 years, at the order of 2 l in 100 years and less than 5 l in 500 years. It is obvious that even if all the brine which has reached the waste cylinder, is consumed by a corrosion process, only a very limited amount of metal can react. This point will be discussed in more detail later in this report.

In a scenario where the water responsible for the corrosion is not originating from brine migration, but from some sort of flooding a greater amount of metal possibly can corrode. The aqueous solution will in this case probably be different from the brine in the former case with respect to chemical composition, pH, oxygen content etc., but again, no detailed information is available at present. As a first approximation it can be calculated how much neutral, oxygen saturated NaCl solution has to pass the waste cylinder in order to dissolve a certain

amount of metal, assuming that oxygen reduction is the cathodic process. The details of this approach will be discussed later.

Although the detailed compositions of the brine in the two above mentioned cases are not available it might be instructive to give the compositions of two brines from the proposed Waste Isolation Pilot Plant (WIPP) in the U.S.A. (see table 1).Brine "A" is a high Mg/K/Na chloride brine and is considered tentatively representative of the minute brine inclusions found in bedded-salt formations. Brine "B" is a near saturated, predominantly NaCl brine representative of dissolved bedded salt at the 800 m horizon of the proposed WIPP site (ref. 4). For comparison also the composition of seawater is given in table 1.

Attention must be called upon the importance of the content of Mg in brine "A". At elevated temperatures hydrolysis of $MgCl_2$ will take place:

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$$

resulting in a reduction of pH and consequently in a more aggressive solution. Experiments have shown (ref. 4) that the pH of brine "A" will decrease from 6,5 to 3,4 if the brine is heated to 250°C and quenched. For seawater the corresponding change in pH is from 8,1 to 3,9. For brine "B", having a very low content of $MgCl_2$, the change in pH is very limited, less than one pH-unit.

In table 2 is given the composition of another brine for which experimental corrosion results are available. This brine occurs at the Salton Sea KGRA, Imperial Valley, California. This brine is high in Na, Ca and K, but low in Mg.

3. Types of corrosion

The type of corrosion is of primary importance for the lifetime of the overpack around the glass cylinder. Uniform corrosion is the least dangerous type of corrosion, because the major part of the metal has to be destroyed before leaks are developing.

Localized corrosion is more dangerous, under unfavourable conditions leading to penetration in much shorter times. One form of localized corrosion is pitting, where the anodic process is concentrated into a number of small areas, while the cathodic process still is taking place over the major part of the surface. A great number of smaller pits will of course be less dangerous than a few, larger pits. Pitting can occur in the majority of metals and alloys (especially in Cl^--solutions), but certain groups of alloys (e.g. aluminium alloys and stainless steels) are more susceptible to pitting than others.

Also stress corrosion cracking (SCC) can lead to failure within comparatively short time. The propagation rate of a crack caused by SCC can vary within very wide limits and for a material which is susceptible to SCC it will be difficult to evaluate the life expectancy with any reasonable accuracy.

In table 3 are listed the types of corrosion that various classes of alloys undergo in concentrated brines (ref. 8).

4. Materials

The choice of material for protection of the glass cylinders must be based upon a number of factors, e.g. corrosion characteristics, price, availability, mechanical properties, technological properties etc. In this section a brief summary of the corrosion characteristics of a few of the most important groups of alloys will be given.

Results from comprehensive systematic examinations of corrosion rates as a function of the relevant parameters (chemical composition of the brine, oxygen content, pH, temperature etc.) are not available. Corrosion rates of a number of alloys (nominal composition, see table 4), tested in the brines mentioned in section 2.2. at temperatures higher than those supposed in the present case, will, however, still be of interest and are given in the tables 5 to 7. The absolute values of the figures given cannot be used as such, but will nevertheless give an impression of the order of magnitude of the possible corrosion rates. The tables also give information on how sensitive the individual alloys are to the oxygen content in the brine. It must be emphasized, however, that the corrosion rates given in the tables are the results of short term experiments (a few weeks) and that the long term corrosion rates are likely to be smaller, even when the limited amount of brine migrating to the metal surfaces not is taken into account. Further it must be remembered that the figures in the tables Nos. 5-7 are referring only to uniform corrosion, giving no information on localized corrosion as pitting, crevice corrosion, stress corrosion cracking etc. Some information, mostly qualitative, on pitting and stress corrosion cracking is given in tables Nos. 8 and 9. Again the results are based on short term experiments at 232°C. A short survey on the anticipated performance of metals in halite brines is given in general terms in table 10.

In the following a few materials will be discussed in somewhat more detail.

4.1. Mild steel

Mild steel is not in itself a very corrosion resistant material, and the corrosion rate will depend very much on the environment, ranging from almost nil to extremely fast rates. In a neutral, oxygen-free solution where hydrogen evolution is the only possible cathodic reaction, the corrosion rate will for most practical purposes be negligible. Thus, in a 4% NaCl solution (oxygen-free, RT, pH more than 5) the corrosion rate of mild steel will be limited to a few /um/year (ref. 6). In acid solutions (pH less than 5) the corrosion rate increases rapidly with decreasing pH and can in strong acids at room temperature be as high as several millimeters or even centimeters per year.

The effect of pH on the corrosion rate is illustrated in fig. 1, where corrosion data on 1010 mild steel are given for several geothermal plants (ref. 8). These data are superimposed on a corrosion-versus-pH curve for the same material in hot seawater. The data clearly show that carbon steels rapidly become less satisfactory as the pH decreases below 5.

Also higher temperatures will result in higher corrosion rates, depending on the composition of the brine. Examples on corrosion rates at higher temperatures (232°C and 250°C) are found in tables 5 and 7. In three different, deaerated brines corrosion rates of 70, 121 and 1700 /um/y are found, while the corrosion rate in deaerated seawater is about 400 /um/y. The large spread in these figures illustrate the influence of the composition of the brine and is probably especially reflecting the differences in pH mentioned earlier.

The combined influence of pH and temperature on the corrosion rate of A 212 B carbon steel in deaerated 4 M Na Cl is in ref. 10 approximated by the expression

$$i_{corr} = 4{,}83.10^{3} \exp.(-3{,}98.10^{3}/T) + 1{,}06.10^{5}.10^{-pH} \exp.(-2{,}10.10^{3}/T)$$

where i_{corr} is the corrosion rate in mm/y and T is the temperature in ^{o}K.

Based on this expression the corrosion rates at various pH-values are shown in fig. 2 as a function of the temperature. The results provide a qualitative and, perhaps, semiquantitative data base for the behaviour of iron and carbon steel in deaerated strong brine solutions. It must be remembered, however, that the results are referring to a situation where the amount of brine is large compared to the steel surface and where the detailed composition of the brine is not modified by radiolysis.

The above mentioned figures all refer to oxygen-free solutions.

As a consequence of the radiation radiolysis of the solution will take place, resulting in the production of oxidizing species (e.g. oxygen), and this will increase the corrosion rate significantly. An example of the influence of the oxygen concentration on the corrosion rate of mild steel at room temperature is shown in fig. 4 (ref. 6). From the diagram to the left it can be calculated that the uniform corrosion rate of steel in an air-saturated solution (165 mg Ca Cl_2/l) at room temperature is of the order of a few tenth's of a millimeter per year which is in good agreement with the experience from atmospheric corrosion and corrosion in seawater. From the diagram to the right it is noticed that the corrosion rate in a saturated solution of Na Cl is remarkably lower than in dilute solutions, reflecting the fact that the solubility of oxygen is decreasing with increasing concentration of Na Cl.

At elevated temperatures and pressures the corrosion rate of mild steel in oxygenated brine is much greater as illustrated in tables 6 and 7, where mild steel and a number of low alloy steels are showing corrosion rates up to a few centimeters per year.

Corrosion rates of that order of magnitude would not be acceptable over an extended period of time, as the required isolation of the waste cylinders for a period

of several hundreds or thousands of years would not be fulfilled. However, such high corrosion rates will actually not be possible in the present case, partly because the expected temperatures are significantly lower than those referred to in tables 6 and 7, but especially because the amounts of brine available for the corrosion process are very limited.

Without going into any details of the corrosion process, the initial total process might be of the types

$$Fe + 2H_2O \longrightarrow Fe(OH)_2 + H_2$$

or $2Fe + 2H_2O + O_2$ (from radiolysis) $\rightarrow 2Fe(OH)_2$.

In both cases two water molecules are needed for the oxidation of one Fe-atom to Fe(+2). Consequently, the amount of iron which can be transformed into corrosion products is limited by the amount of water available, the theoretical maximum value of the weight ratio Fe/H_2O being $\frac{56}{36}$ or 1,56. If some of the Fe-atoms are oxidized to Fe(+3), the ratio will be even lower.

If migration along the thermal gradient is the only mechanism transporting brine to the waste cylinders, only a few liters per meter will reach the metal surface over a period of 500 years (ref. 3). If the corrosion is completely uniform, the resultant depth of attack will be less than 1 mm, which is insignificant compared to the total thickness of the steel casing, being in the range of 100 - 200 mm. The upper limit of the depth of the attack as a function of the available amount of water under the assumption of uniform corrosion is given in table 11.

However, it is more likely that a certain degree of pitting will take place rather than that the corrosion should be completely uniform. The total corrosion will still be controlled by the amount of water available, i.e the same as in the case of uniform corrosion. The depth of penetration will depend on the shape of the pits and of the

number of pits per meter.

Under the assumption that the pits are hemispherical with a radius of r mm, the weight of the iron corroded away from one pit is

$$\frac{1}{2} \cdot \frac{4}{3} \pi r^3 \cdot 0{,}0078 = 0{,}01634\ r^3\ g$$

corresponding to a minimum amount of water of $0{,}0105 . r^3$ g.

If the total amount of water available is x g and the corrosion is distributed on n identical pits, the pitting depth r can be calculated from the equation

$$x = n \cdot 0{,}0105 \cdot r^3$$

The results are given in table 12 and in fig. 3.

In practice the attack will probably be a combination of pitting and uniform corrosion and the depth of the pitting will therefore be less than that given in table 12.

It is well known that SCC of mild steel will occur only under conditions different from those existing around the waste cylinders stored in salt domes (e.g. in hot concentrated alkaline solutions or in hot concentrated nitrate solutions) and, therefore, the problem of SCC needs not to be taken into consideration.

Therefore, it can be concluded that if the amount of brine available for corrosion during a period of e.g. 500 years is limited by the migration mechanism to a few liters per meter (e.g. less than ten liters per meter), then a steel overpack, having a wall thickness of at least 10 to 15 cm, will remain intact during that period. This conclusion is based on very conservative assumptions.

If in the period of interest the steel overpack is exposed to significantly larger amounts of brine, e.g. as a consequence of inundation, the situation is less clear and the very conservative approach given above cannot be used. The corrosion rate will depend on a number of parameters (qualitative and quantitative composition of the solution,

pH, temperature, radiolysis etc.) and can as already mentioned earlier vary over several decades. Therefore, under these conditions a reasonable estimate of the expected lifetime cannot be given.

However, it might nevertheless be useful to give an estimate of how much brine (in equilibrium with the atmosphere) is needed to react with a certain amount of steel under the assumption that reduction of dissolved oxygen is the only significant cathodic reaction.

The solubility of oxygen (1 atm.) in saturated Na Cl at RT is about 1 ml O_2(STP)/l or about 1,4 mg O_2/l (ref. 11). Consequently, saturated Na Cl in equilibrium with air will contain approximately 0,3 mg O_2/l. According to the equation

$$2\ Fe + 2H_2O + O_2 \longrightarrow 2\ Fe(OH)_2$$

the iron/oxygen ratio is $\frac{56}{16} = 3{,}5$, and, consequently, the oxygen dissolved in 1 liter of saturated Na Cl can react with about 1 mg Fe. Although the detailed presuppositions can be discussed, it is obvious from this calculation, that very large volumes of Na Cl solution are needed if the steel overpack shall be seriously attacked by the oxygen dissolved in the brine. Thus to react with the first millimeter of a 60 cm diameter steel cylinder, 15,000 m^3 air-saturated brine are needed per meter of the cylinder. It is difficult to see how these enormous amounts of brine should be transported to the surface of the cylinder, but a discussion of this question is outside the scope of this report.

4.2. Austenitic stainless steels

The austenitic stainless steels of the 300 series show a significantly lower uniform corrosion rate than carbon steels and low alloy steels because of their high tendency to passivity. However, chlorides are effective in destroying the passive film, initiating a pitting attack. When pitting has started, the steel is often penetrated faster than would be the case if there were uniform corrosion of

carbon steel under the same conditions.

Austenitic stainless steels are also susceptible to stress corrosion cracking in chloride environments, especially at somewhat elevated temperatures. Propagation of the cracks can be fast, and penetration can occur within a very short time, e.g. a few weeks. Because of these two weaknesses, pitting and SCC, the austenitic stainless steels must be considered as unsuitable for use in the environment of interest in the present case.

4.3. Ferritic stainless steels

The common ferritic stainless steels with Cr-contents in the range 12 - 18% Cr are more susceptible to pitting and crevice corrosion than the austenitic steels and will therefore be of less interest although they have the advantage of being virtually insusceptible to SCC. Ferritic steels with very high Cr-contents (i.e. 25 - 30% Cr) and a few percent of Mo seem to have a high resistance to corrosion in hot deaerated brine but is less resistant if oxygen is introduced into the brine (see tables 6,7, 8 and 9).

4.4. Ni-base alloys

In deaerated hot brine the uniform corrosion rate of most Ni-base alloys is very low (see tables 5 and 7), these alloys (e.g. Inconel 625 and some of the Hastelloys) belonging to the most resistant alloys. Experiments at about 230°C have shown, however, that if oxygen is introduced in the brine, the corrosion resistance is significantly reduced, both pitting and SCC being observed (see tables 7, 8 and 9). The behaviour will probably be better, possibly acceptable, at lower temperatures (e.g. 100°C), but is not known in detail and further experiments are required.

However, the potential risk of localized corrosion combined with the comparatively high price will probably make the choice of these alloys less attractive.

4.5. Copper

Copper is a comparatively noble metal which is thermodynamically stable in oxygen-free water and in non-oxidizing solutions. In the Swedish KBS-study copper has been proposed as container material for disposal of non-reprocessed fuel elements (ref. 7). If oxygen is present (e.g. from radiolysis) corrosion can occur, possibly in the form of pitting or crevice corrosion. Copper is not sensitive to SCC and hydrogen embrittlement will not occur at the temperatures foreseen. The corrosion will be controlled by the amount of oxygen available and a considerable lifetime will therefore be expected. In the KBS-study a maximum pitting rate of 0,04 mm per year is assumed, resulting in a lifetime of more than 5000 years for a container with a wall thickness of 200 mm.

4.6. Titanium and titanium alloys

Titanium or titanium alloys are very promising materials for use in brines from a corrosion point of view. Ti-alloys are not thermodynamically stable under these conditions, but they are protected by a very resistant oxide layer, resulting in negligible corrosion rates and high resistance to pitting and SCC. The great tendency to passivity is illustrated by the potential-pH-diagram shown in fig. 5. The very low uniform corrosion rates found at short term experiments at high temperatures are given in tables 5, 6 and 7. In ref. 7 is referred to a number of experiments in seawater (60 - 90^{o}C) and in soil with a high content of chloride and a low pH. These experiments, having durations from 6 months to 8 years, all resulted in extremely low corrosion rates, corresponding to a few tenth's of a millimeter over a period of 1000 years.

Under certain conditions (depending on temperature, pH, Cl^--concentration, oxidants etc.) localized corrosion as pitting and crevice corrosion can occur. Unalloyed Ti seems in this respect to be more sensitive than some of the Ti-alloys. Some of the experiences with localized

corrosion of Ti in chloride solutions are given in figs. 6, 7, 8, 9 and 10. According to this information unalloyed Ti should be immune to pitting up to temperatures of about 70°C, while Ti - 0,2% Pd should be immune up to about 110° C. Above these temperatures pitting might possibly occur in metal-to-metal crevices. However, pitting will only be probable at temperatures above 150°C for unalloyed Ti and above 180°C for Ti - 0,2% Pd.

Although this information is based on experience over a limited period of time it seems reasonable to conclude that a Ti-alloy would be an appropriate choice if corrosion has to be minimized even at the presence of abundant amounts of water and oxygen (or other oxidants). The specific choice of the Ti-alloy will require a closer consideration.

4.7. Combinations of materials

A technical and economical advantage can possibly be obtained by using a combination of materials, e.g. a thick layer of a comparatively cheap material combined with a thinner layer of a more expensive, but also more corrosion resistant material. An example of such a combination is the Swedish proposal in the KBS study, where the vitrified waste cylinder is shielded by a 100 mm layer of lead protected on the outside by a 6 mm titanium capsule. The canisters are foreseen to be placed in vertical drill-holes in rock, 500 m below ground, and embedded in a buffer of 80 - 90% sand and 20 - 10% bentonite (ref. 7). In the Swedish study the life of a titanium canister with a lead lining is estimated to have a life of at least thousands of years, even in the case of inundation with water from the Baltic Sea.

In this example the protection is based primarily on the titanium layer, having a corrosion potential more noble than that of lead and being the most corrosion resistant of the two. In case of a penetration of the titanium layer (due to mechanical damage or localized corrosion), the exposed lead could suffer from localized attack. The corrosion

rate of the lead would then be determined by the supply of oxygen from the surroundings to the canister surface, but it is estimated that perforation of the 100 mm thick lead lining will take 4000 - 5000 years. The titanium will in this case be polarized cathodically, but will not reach the critical potentials where hydrogen uptake will take place. Hydrogen embrittlement of the titanium will therefore not occur.

In the proposed combination of titanium and lead as materials for corrosion protection and shielding, lead could probably be substituted by steel, being a cheaper material. The consequences with respect to shielding are outside the scope of this report, but the corrosion aspects have to be evaluated. In case of penetration of the outer titanium layer, the situation will be parallel to the former case. Steel will, like lead, be anodic to titanium and, consequently, accelerated corrosion of steel will take place. The corrosion resistance of steel is less than that of lead, but again, the corrosion rate will probably be controlled by the amount of oxygen available.

Instead of using the more noble and corrosion resistant material as the outer layer as proposed in the Swedish study, one could consider the possibility of interchanging the two layers, having the less noble material, e.g. steel, as the outer layer. In the first long period the situation would be identical to that already discussed in chapter 4.1. The corrosion would be controlled by the environment and the available amount of brine would set an upper limit to the total amount of corrosion.

If abundant amounts of water for some reason should be available, the corrosion will continue and, eventually, penetration of the steel layer will occur. If the corrosion is completely uniform, almost the total amount of steel shall have reacted before penetration takes place, and the life time of the steel layer will probably be hundreds of years or more. However, it is more likely that the attack will be non-uniform and that penetration will occur in a shorter time. When corrosion has advanced to the more noble

metal (e.g. titanium or (possibly better) copper), this metal will be cathodically protected by the steel, the penetration will stop and the corrosion will instead spread to the remaining steel. That means that even in the case of non-uniform corrosion most of the steel has to be consumed before the next barrier (the more noble metal) is attacked. The situation is now similar to that discussed in chapters 4.5 or 4.6 and the remaining life-time might still be very long.

Also the combination of steel and lead could be considered. Here again steel is the less noble of the two metals and lead will to a certain degree be protected when coupled to steel. On the other hand, lead is close to steel in its electrochemical character, the difference in corrosion potential in a saturated NaCl-solution being only at the order of 50 mV (based on short term experiments (few days)). Consequently, the galvanic effect will be of a limited magnitude (ref. 14) and the combination of steel and lead will probably be of less interest than the combinations mentioned above.

5. Discussion and conclusion

The primary safety against spreading of the high-level radioactive waste from the repository to the biosphere must primarily be based on the geological stability of the salt domes, on the low leaching rates of radioactive isotopes from the glass cylinders and on the very limited transport possibilities in the salt dome. However, an additional delaying step can be introduced by using a more or less corrosion resistant overpack on the waste cylinder.

The delay which can be obtained (i.e. the life time of the overpack) will depend on the material chosen and on the environment. As to the material two factors will be of importance:

1) Resistance to general corrosion
2) Resistance to localized corrosion, e.g. SCC.

While the general corrosion is a comparatively slow process, which furthermore probably will be controlled by the very limited amount of electrolyte available, the localized corrosion (especially SCC) under unfavourable conditions can ruin the integrity of the overpack in a short time. Consequently, a number of alloys, which under certain conditions have shown to be sensitive to SCC, have to be ruled out in spite of the fact that their resistance to general corrosion is known to be excellent. This is the case for the austenitic stainless steels and possibly also for a number of high nickel alloys. Copper and titanium (or Ti-alloys) combine a good resistance to general corrosion with a good resistance to localized corrosion and should be considered as candidate materials for the protective overpack. In spite of the fact that the corrosion resistance of steel is rather limited, mild steel or a low alloy steel should nevertheless be taken into consideration because (as mentioned above) the corrosion probably will be controlled by the limited amount of brine available.

A favourable combination could be an inner layer of a corrosion resistant metal as copper or titanium surrounded by a thicker layer of steel. If the steel contrary to expectation should be penetrated by corrosion (e.g. pitting), the attack will stop when reaching the more noble metal and spread to the remaning steel which has to be consumed before corrosion will take place on the inner layer. The inner layer will now yield protection for an extended period.

Whether to use copper, titanium or possibly another metal or alloy for the inner layer needs closer consideration and a possible recommendation ought to be based on further experimental examinations, preferably after the environment is better defined than at present. This will also give a better platform for a more realistic estimate of the life expectancy.

References

1. F. Hasted and S. Mehlsen: Design and Safety Evaluation of a Danish High-Level Waste Disposal Facility in Selected Salt Domes. IAEA-SM-243/154.

2. N. Laursen, Elkraft, personal communication.

3. H. Neltrup: Heat gradient induced migration of brine inclusions in rock salt. Mathematical treatment. RP-15-79. Risø, October 1979.

4. J.W. Brathwaite and M.M. Molecke: High-Level Waste Canister Corrosion Studies Pertinent to Geologic Isolation. SAND 78-2111 (December 1978).

5. P.B. Needham, Jr. et al.: Corrosion Studies in High-Temperature, Hypersaline Geothermal Brines. Paper No. 59, Corrosion /79, Atlanta, U.S.A.

6. W. Schwenk: Verhalten des Stahles bei chemischer Beanspruchung (in Werkstoffkunde der gebräulichen Stähle, Verein Deutscher Eisenhüttenleute, 1977).

7. KBS Teknisk Rapport 31. Bedömning av korrosionsbeständigheten hos material avsedda för kapsling av kärnbränsleavfall (1977).

8. W.D. Ludemann, L. Abrego, P.D. McCright: Corrosion Studies on Retrievable Spent Fuel Containers. UCID-17917 (December 1978).

9. KBS Teknisk Rapport 107. Blyinfodrad titankapsel för upparbetat og glasat kärnbränsleavfall. Bedömning ur korrosionssynspunkt. (25-5-1978).

10. F.A. Posey, A.A. Palko and A.L. Bacarella: Corrosivity of geothermal brines. ORNL/TM-6159 (Nov. 77).

11. Gmelin: Sauerstoff, Lieferung 3, p. 478 (1958).

12. G. Wranglén: Metallers korrosion och ytskydd. Almqvist & Wiksell, Stockholm, 1967.

13. KBS Teknisk Rapport 11. Sture Henriksson, Kjell Pettersson: Utredning rörande titans lämplighet som korrosionshärdig kapsling för kärnbränsleavfall (1977).

14. F.L. LaQue and H.R. Copson (ed.): Corrosion resistance of metals and alloys. Reinhold, New York (1963).

TABLE 1 (ref. 4)

REPRESENTATIVE SOLUTION COMPOSITIONS
(major ions)

Ion	Seawater (ppm)	Brine A (ppm)	Brine B (ppm)
Na^+	10,651	42,000	115,000
K^+	380	30,000	15
Mg^{+2}	1,272	35,000	10
Ca^{+2}	400	600	900
Sr^{+2}	13	5	15
Cl^-	18,980	190,000	175,000
SO_4^{-2}	884	3,500	3,500
I^-	.05	10	10
HCO_3^-	146	700	10
Br^-	65	400	400
BO_3	-	1200	10
pH	8.1	6.5	6.5
Total Dissolved Solids:	35g/l	306g/l	297g/l

TABLE 2 - Composition of synthesized Salton Sea KGRA-type brine (ref. 5)

Constituents	Composition, ppm[1]
Na	53,000
Ca	28,800
K	16,500
Fe	2,000
Mn	1,370
Zn	500
Sr	440
SiO_2	400
B	390
Ba	250
Le	210
Pb	80
Rb	70
Cs	20
Mg	10
Cl	155,000
S	30
CO_2	500
pH	Adjusted to 6.1 w/NaOH

[1]Based on Helgeson's analysis of IID #2.

TABLE 3. Morphology of corrosion attack in concentrated brines.

Type of corrosion	Causative environment	Susceptible alloys
General (metal wastage)	All brines	Mild steels Low-alloy steels
Localized (pitting and crevice)	Oxiding brines Acidified or unmodified brines	Cu alloys All steels, especially Cr-steels Ni and Ti alloys (under some conditions)
Intergranular	Oxidizing environments, usually	Ferritic and austenitic stainless steels Ni alloys in sensitized condition
Stress corrosion cracking	All brines	Austenitic SS, especially
Hydrogen embrittlement	Brines with low pH	High-strength alloy steels Martensitic SS

TABLE 4 (ref. 4)

NOMINAL CHEMICAL COMPOSITION OF CANDIDATE ALLOYS

Alloy	C	Mn	Si	Cr	Ni	Mo	Fe	Cu	Others
1018 Mild Steel	.18	0.75	0.25	-	-	-	Bal	-	-
4130 Carbon Steel	.3M[a]	0.5	.3	1.0	-	.2	Bal	-	-
Corten A Steel[e]	.1	0.4	0.5	1.0	-	-	Bal	-	.02Ti
2 1/4 Cr-1 Mo	.2	0.8	0.3	2.2	-	1	Bal	-	-
Naval Brass	-	-	-	-	-	-	-	60	39Zn,1Sn
90-10 Cupronickel	-	-	-	-	10	-	1.3	88.7	-
SS-304	.08M	2.0M	1.0M	19	10	-	Bal	-	-
SS-316	.08M	2.0M	1.0M	17	12	2.5	Bal	-	-
SS-Nitronic 50[g]	.06M	5	-	22	13	2.25	Bal	-	.2Nb,.2V
SS-20-Cb3[b]	.07M	2.0M	1.0M	20	34	2.5	Bal	3.5	-
SS-Ebrite 26-1[d]	.01M	0.4M	0.4M	26	0.5M	1	Bal	0.2M	-
Monel 400[a]	.2	1.0	0.2	-	66.5	-	1.2	31.5	-
Incoloy 825[a]	.03	0.5	0.2	21.5	42	3.0	30	2.2	0.9Ti
Inconel 600[a]	.04	0.20	0.20	15.5	76.0	-	8.0	-	-
Inconel 625[a]	.05	0.2	0.2	21.5	63	9.0	2.5	-	4Nb;0.2Ti
Hastelloy C-276[c]	-	-	-	15	59	.7	5	-	4W
Zircaloy 2	.12	-	-	0.1	0.05	-	-	-	1.5Sn,98.2Zr
Titanium, C.P.	-	-	-	-	-	-	-	-	99.5Ti
Ticode 12[f]	.012	-	-	-	0.84	0.34	.09	-	98.9Ti
MP35N	-	-	-	20	35	10	-	-	35Co

[a]M denotes maximum
Trademarks: [a]Huntington Alloys; [b]Carpenter Technology Corp; [c]Cabot Corp; [d]Allegheny Ludlum Industries; [e]U.S. Steel; [f]TIMET; [g]Armco Steel Corp

TABLE 5 (ref. 4)

CORROSION RATES OF CANDIDATE ALLOYS IN DEOXYGENATED SOLUTIONS (250°C, P = 5MPa)

Alloy	Brine A (mm/yr)	Brine B (mm/yr)	Seawater (mm/yr)
1018 Mild Steel	1.7	0.07	0.4
Corten A Steel	0.9	0.05	0.2
2 1/4 Cr-1 Mo Steel	1.0**	0.1**	0.2
Lead	0.5	0.3	0.3
Copper	0.07	0.05	0.05
Naval Brass	1.0	-	1.0
90-10 Cupronickel	0.14	-	0.07
SS-304L	0.018	0.01	0.006
SS-316L	0.015	-	0.005
SS-Nitronic 50	0.008	-	0.003
SS-20Cb3	0.007	-	0.005
SS-Ebrite 26-1	0.016	-	0.005
Monel 400	0.03	-	0.1
Incoloy 825	0.006	-	0.004
Inconel 600	0.009	0.007	0.005
Inconel 625	0.005	0.001	0.012*
Hastelloy C-276	0.007	-	0.0015
Zircaloy-2	0.001	-	-
Titanium C.P.	0.003	-	0.006
Ticode 12	0.0006	-	0.005

*pitting corrosion; **crevice corrosion

TABLE 6 (ref. 4)

CORROSION RATES OF CANDIDATE ALLOYS IN OXYGENATED SOLUTIONS (250°C and P=7MPa) (O_2)=600 ppm in Brine A and 1750 ppm in Seawater.

Alloy	Brine A (mm/yr)	Seawater (mm/yr)
1018 Mild Steel	7.0	11.0
Copper	1.2	5.0
Lead	1.2	1.0
90-10 Cupronickel	0.4	0.7
SS-Ebrite 26-1	0.24	-
SS-20Cb3	0.1**	-
Inconel 600	-	0.1
Hastelloy C-276	0.06*	0.2*
Ticode 12	0.004	-

* pitting and crevice corrosion
**crevice corrosion

TABLE 7 - General corrosion rate in Salton Sea KGRA-type brine at 232° C (ref. 5)

Metal	Corrosion Rate, μm/y 15-day exposure			
	Deaerated	100 ppm O_2	100 ppm CH_4	250 ppm CO_2
Iron Based:				
Sandvik 3Re-60	51	-	-	-
E-Brite 26-1	3	528	0	5
316 L SS	0	6,220	0	5
Carpenter 20 SS	8	-	-	-
1020 carbon steel	121	26,900	61	-
4130 steel	96	25,400	84	-
Cor-Ten B	33	30,000	10	46
Mariner	41	33,300	38	213
430 SS	0	8,760	0	-
Nickel based:				
Monel 400	43	7,320	0	23
Inconel X-750	8	-	-	-
Inconel 625	0	488	2	23
Hastelloy S	0	-	-	-
Hastelloy G	3	-	-	-
Hastelloy C-276	0	152	0	-
Copper based:				
70-30 cupronickel	86	5,720	76	253
Titanium based:				
Titanium	8	0	0	0
Ti-1.7W	0	-	-	-
Ti-2Ni	3	0	-	-
Ti-10V	0	-	-	-
Ti-0.2Pd	0	0	0	0
TiCode-12	-	0	0	-
Molybdenum based:				
TZM	15	-	-	-

[1]Dash (-) = not tested.

TABLE 8 - Pitting corrosion in Salton Sea KGRA-type brine at 232° C[1,2] (ref.5)

Metal	15-day exposure			
	Deaerated	100 ppm O_2	100 ppm CH_4	250 ppm CO_2
Iron based:				
Sandvik 3RE60	N	-	-	-
E-Brite 26-1	N	927	760	D
316 L SS	N	D	N	N
Carpenter 20 SS	D	-	-	-
1020 carbon steel	127	D	N	-
4130 steel	N	-	D	-
Cor-Ten B	D	N	N	D
Mariner	N	N	N	D
430 SS	N	D	1,400	D
Nickel based:				
Monel 400	D	D	N	D
Inconel X-750	N	-	-	-
Inconel 625	N	13,500	N	N
Hastelloy S	N	-	-	-
Hastelloy G	D	-	-	-
Hastelloy C-276	N	318	N	N
Copper based:				
70-30 cupronickel	N	D	N	N
Titanium based:				
Titanium	2540	N	N	N
Ti-1.7W	N	-	-	-
Ti-2Ni	N	-	-	-
Ti-10V	N	-	-	-
Ti-0.2Pd	N	N	N	N
TiCode-12A	-	N	N	-
Molybdenum based:				
TZM	N	-	-	-

[1]Extent of pitting indicated as a pitting rate in μm/y or as follows:
N = not detected.
D = detected.
[2]Dash (-) = not tested.

TABLE 9 - Stress corrosion in Salton Sea KGRA-type brine at 232° C[1,2] (ref. 5)

Metal	15-day exposure							
	Deaerated		100 ppm O_2		100 ppm CH_4		250 ppm CO_2	
Iron based:								
Sandvik 3RE60	25	D	-		-		-	
E-Brite 26-1	3	ND	997	ND	0	ND	0	ND
316 L SS	5	D	2,060	D	0	D	0	D
430 SS	0	D	8,750	D	0	D	8	D
Carpenter 20 SS	8	D	-		-		-	
1020 carbon steel	56	ND	-		53	ND	-	
4130 steel	262	ND	-		-		-	
Nickel based:								
Monel 400	305	ND	-		86	ND	-	
Inconel X-750	10	ND	-		-		-	
Inconel 625	0	ND	569	D	0	ND	0	ND
Hastelloy S	0	ND	-		-		-	
Hastelloy G	10	ND	-		-		-	
Hastelloy C-276	3	ND	287	D	0	D	0	ND
Copper based:								
70-30 cupronickel	198	ND	-		-		-	
Titanium based:								
Titanium	13	ND	3	D	0	ND	13	ND
Ti-1.7W	0	ND	-		-		-	
Ti-2Ni	5	ND	0	ND	-		-	
Ti-10V	0	ND	-		-		-	
Ti-0.2Pd	0	ND	3	D	0	ND	0	ND
TiCode-12A	-		-		0	ND	-	
Molybdenum based:								
TZM	20	ND	-		-		-	

[1]Stress corrosion indicated by:
D = detected.
ND = not detected.
Numbers indicate general corrosion rate of SCC speciments in μm/y.
[2]Dash (-) = not detected.

TABLE 10 Anticipated performance of metals in halite brines. (ref. 8)

Metal	Performance
Iron and carbon steel	High metal wastage rate; may pit or perforate at high temperature. Susceptible to hydrogen embrittlement at low pH.
Silicon cast irons	Much-improved corrosion resistance; poor thermal shock resistance. Limited to cast geometries.
400 series stainless steels	Pitting susceptibility, especially with Cr content <30 wt %. May stress crack (hydrogen embrittle) or corrode intergranularly.
300 series stainless steels	Very susceptible to stress corrosion. May pit, corrode intergranularly.
Super stainless steels (Cr > 20%, Ni > 30%)	Investigate for pitting, intergranular and stress corrosion.
Nickel and nickel alloys	Investigate for pitting, intergranular and stress corrosion.
Aluminum alloys	Very susceptible to pitting attack and stress corrosion.
Copper alloys	Metal wastage at high chloride concentrations, pitting attack under oxidizing conditions.
Titanium and titanium alloys	May corrode or pit in concentrated chlorides at low pH and reducing conditions. Special welding conditions necessary.
Molybdenum, Zirconium, Tantalum	Excellent corrosion resistance in concentrated chlorides, but high cost; may hydrogren embrittle at low pH values.

Table 11 - Uniform corrosion of a steel cylinder (D = 60 cm).

g H_2O/m	max. reacted g Fe/m	depth of attack in µm
200	312	21
500	780	53
1000	1560	105
2000	3120	210
3000	7800	530
10.000	15600	1050

Table 12 - Pitting. (Identical, hemispherical pits).

g H_2O/m	max. reacted g Fe/m	pit depth in mm's			
		1 pit/m	10 pits/m	100 pits/m	1000 pits/m
200	312	27	12	5,6	2,7
500	780	36	17	7,8	3,6
1000	1560	46	21	9,8	4,6
2000	3120	58	27	12,4	5,8
5000	7800	78	36	16,8	7,8
10.000	15600	98	46	21,2	9,8

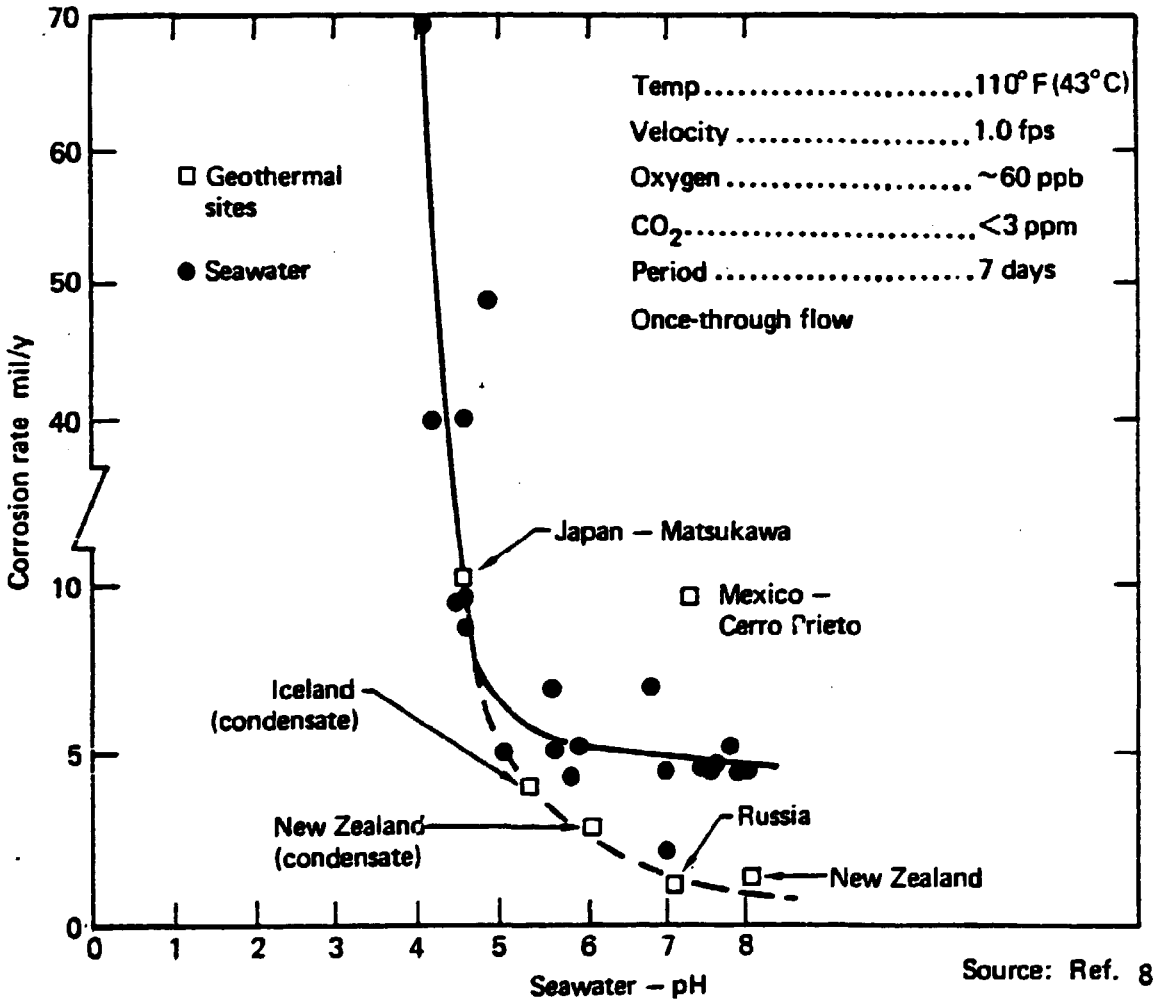
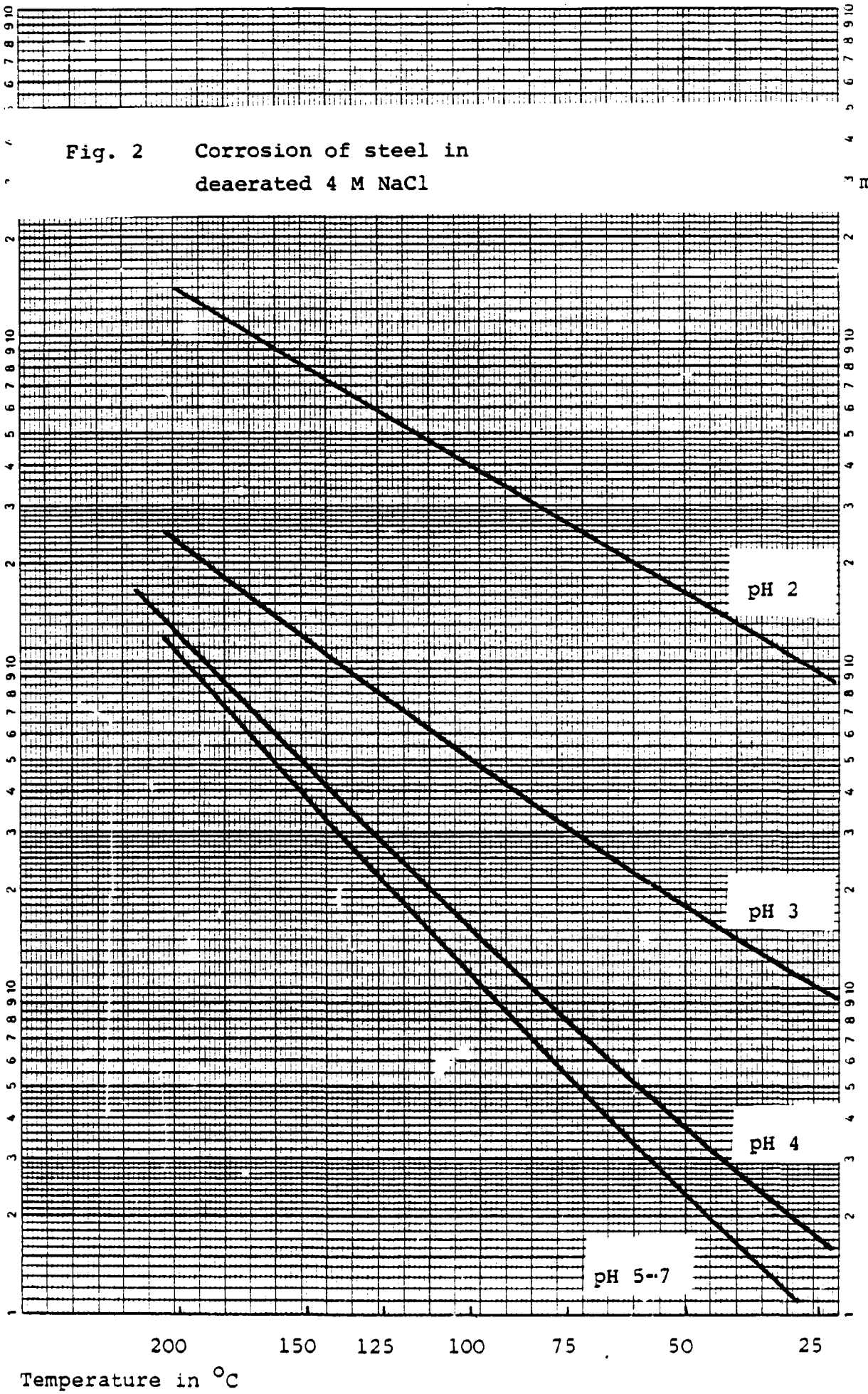


FIG. 1 Effect of pH on the corrosion rate of 1010 mild steel.

Fig. 2 Corrosion of steel in deaerated 4 M NaCl



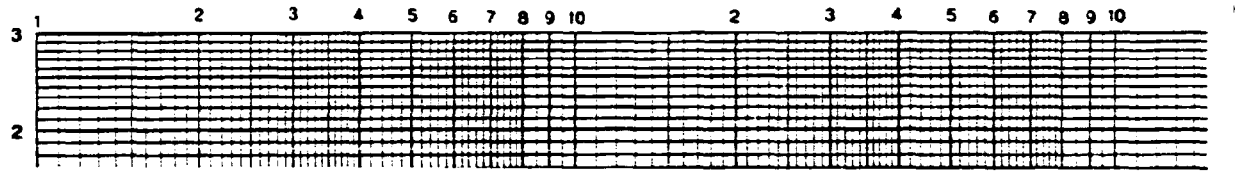
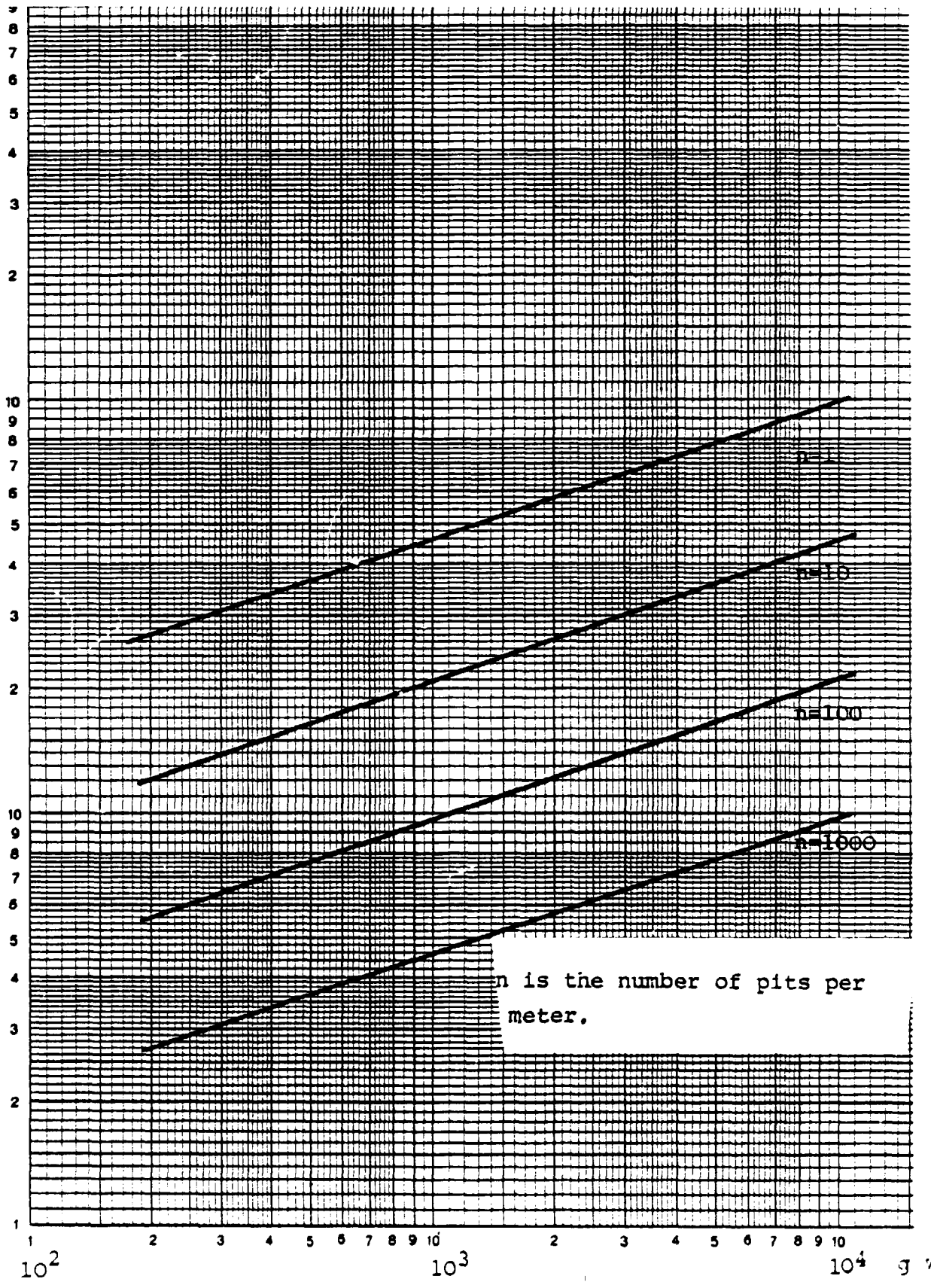


Fig. 3 Maximum depth of identical pits on steel cylinder surface



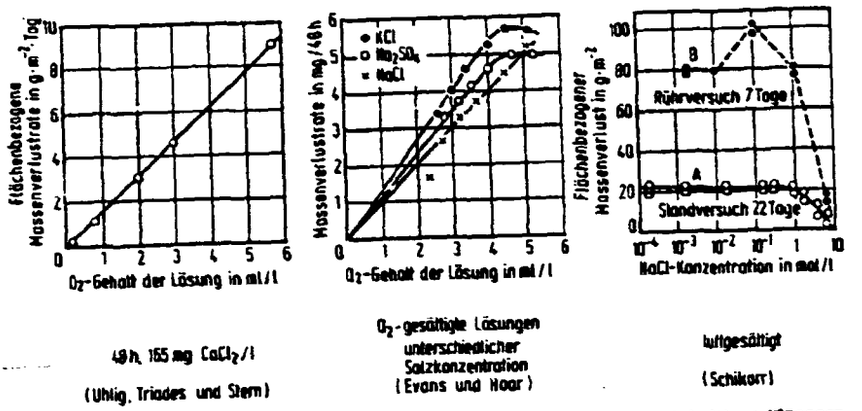


Fig.4 Einfluß des Sauerstoffgehaltes auf die Korrosion in neutralen salzhaltigen Wässern (ref. 6)

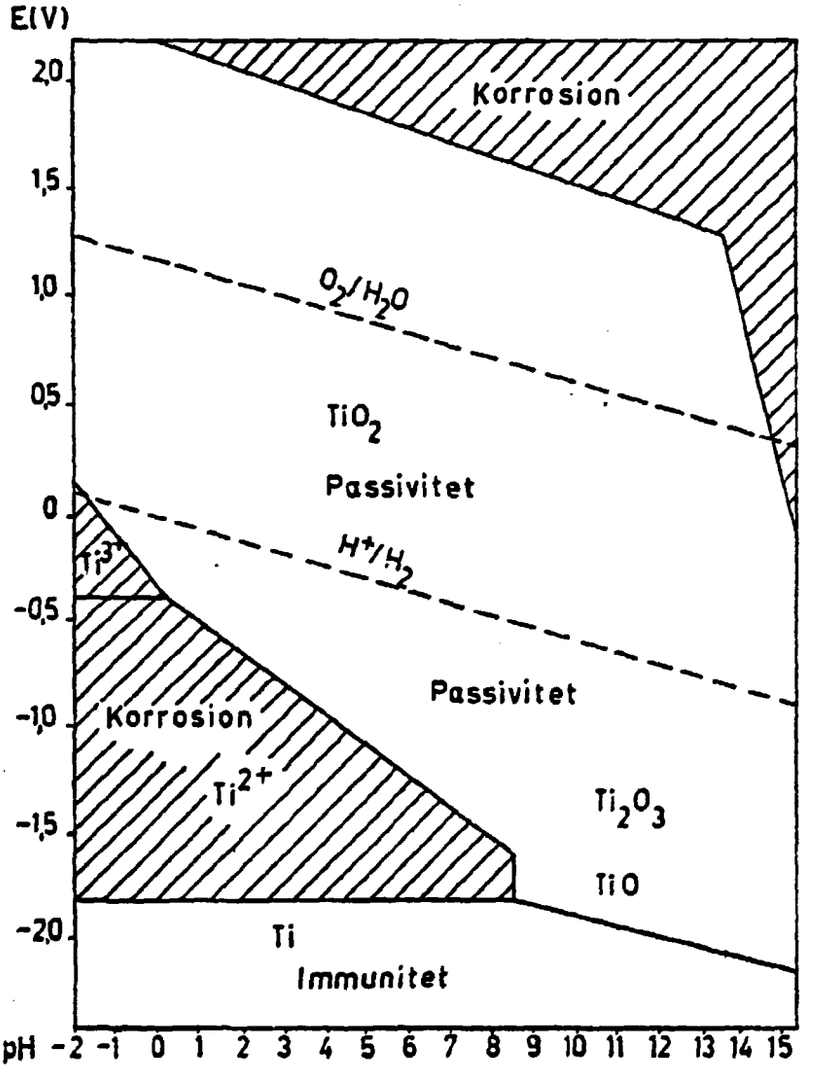
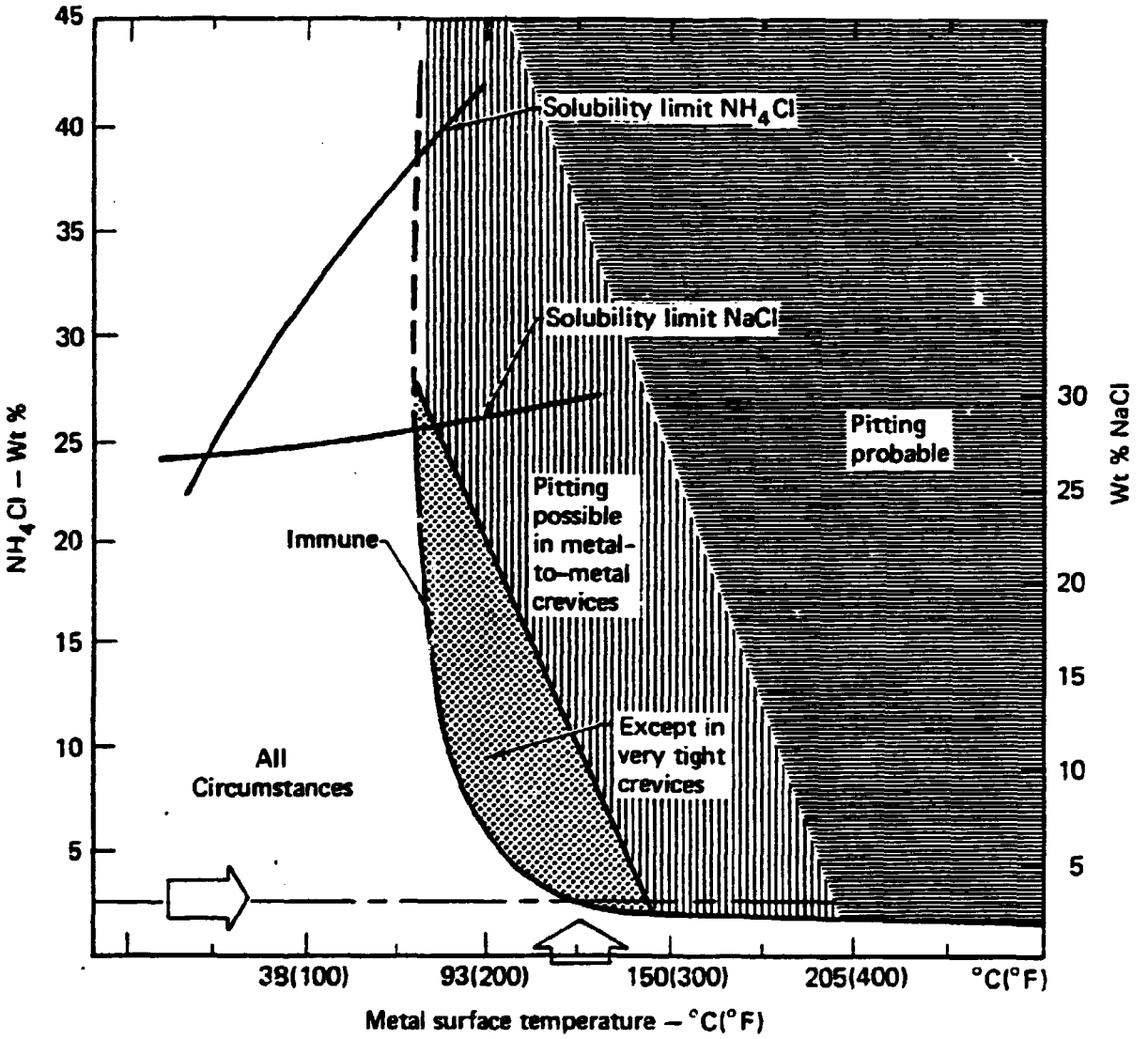


Fig.5 Potential-pH diagram for titanium (ref. 12)



Source: Ref. 8

FIG. 6 Anticipated performance of unalloyed Ti in chloride brines and under NaCl or NH_4Cl deposits.

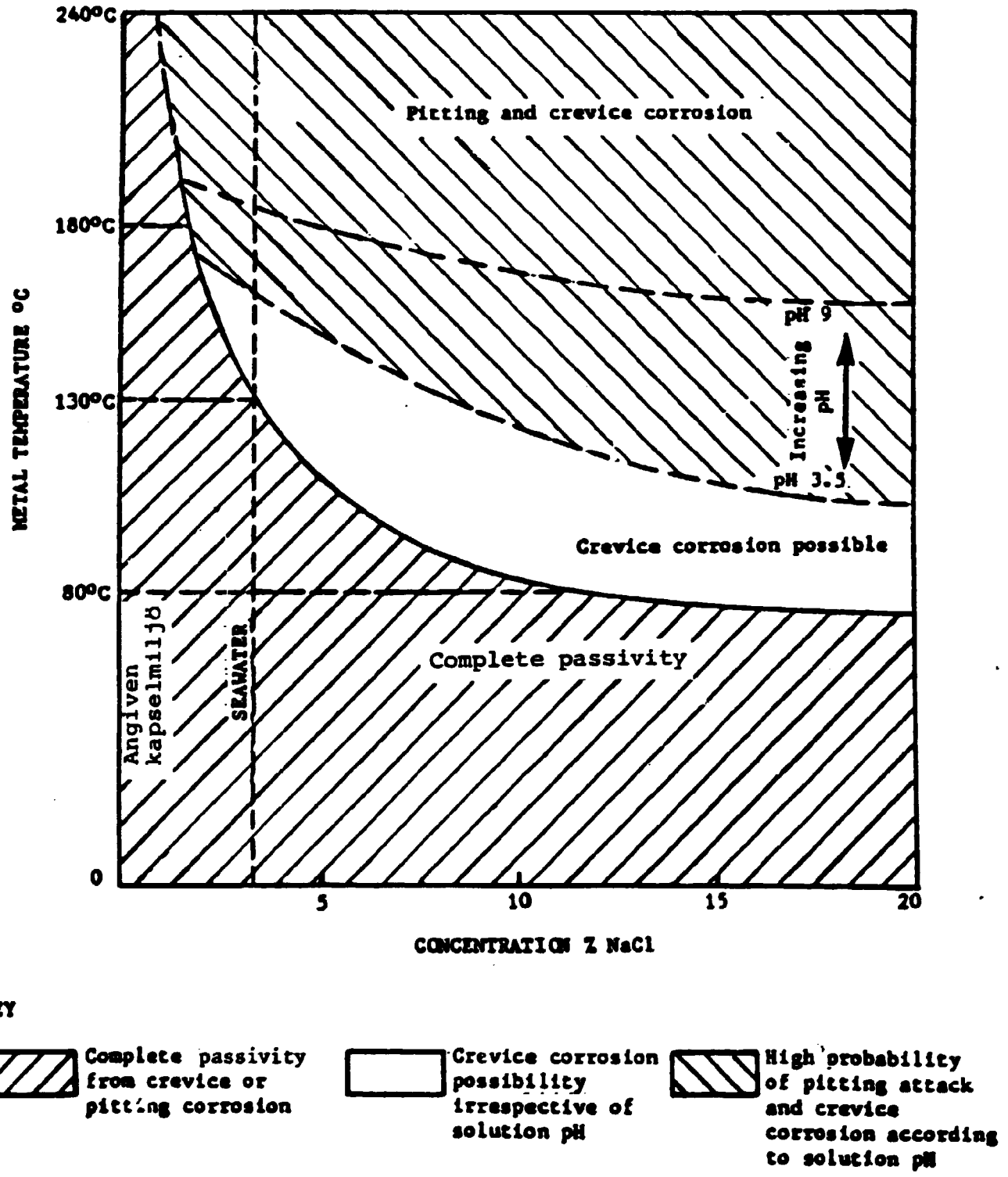


Fig. 7 Inverkan av temperatur, koncentration och pH på spaltkorrosion och punktfrätning hos olegerat titan i havsvatten och koncentrerade kloridlösningar (ref. 7).

Fig. 8 Inverkan av temperatur och koncentration på spaltkorrosion och punktfrätning hos Pd-legerat titan i havsvatten och koncentrerade kloridlösningar (ref. 13).

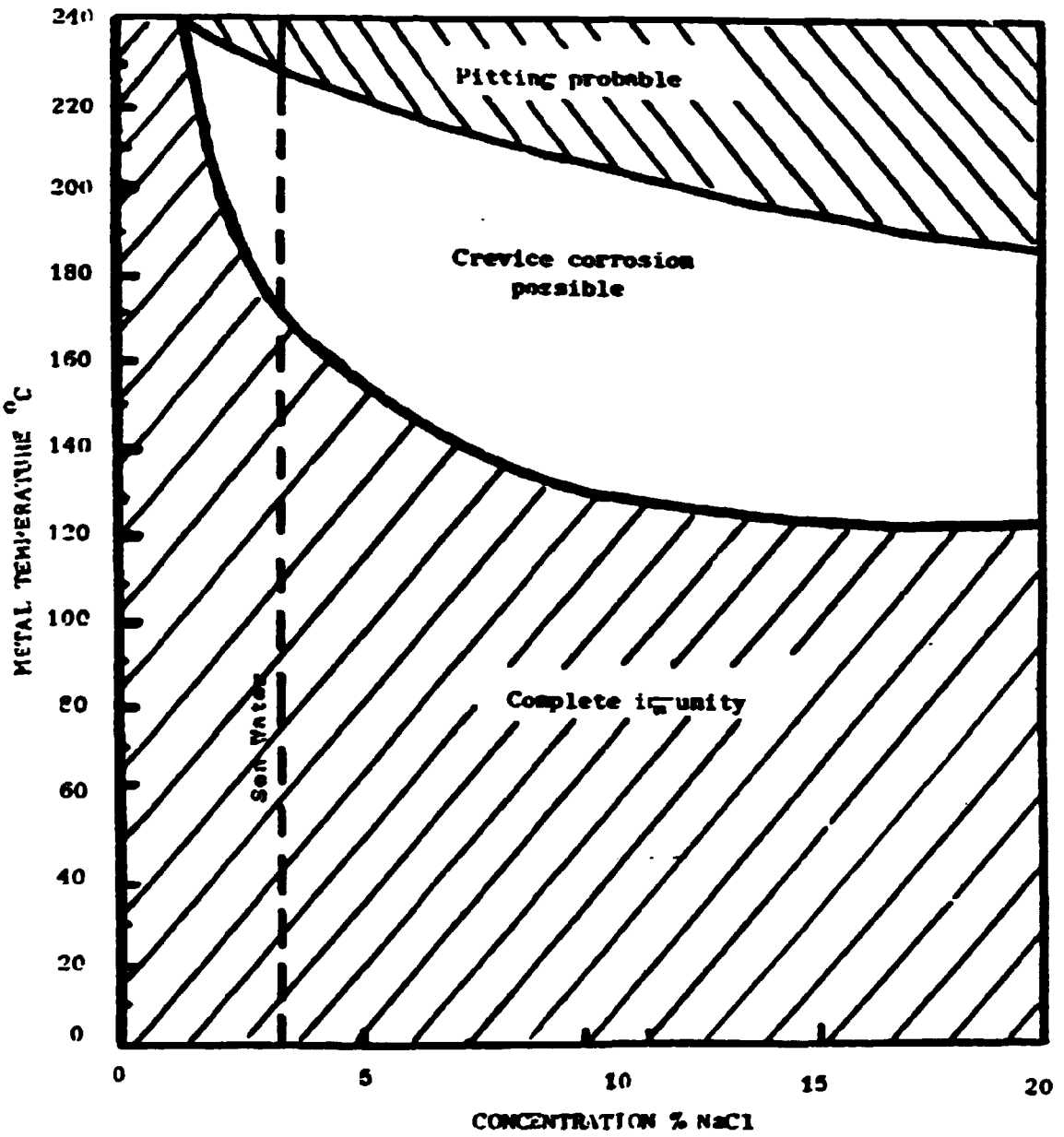


Fig. 9. Corrosion of Ti-50A in Brine Solutions 24% NaCl (ref. 7)

x = corroded
o = not corroded

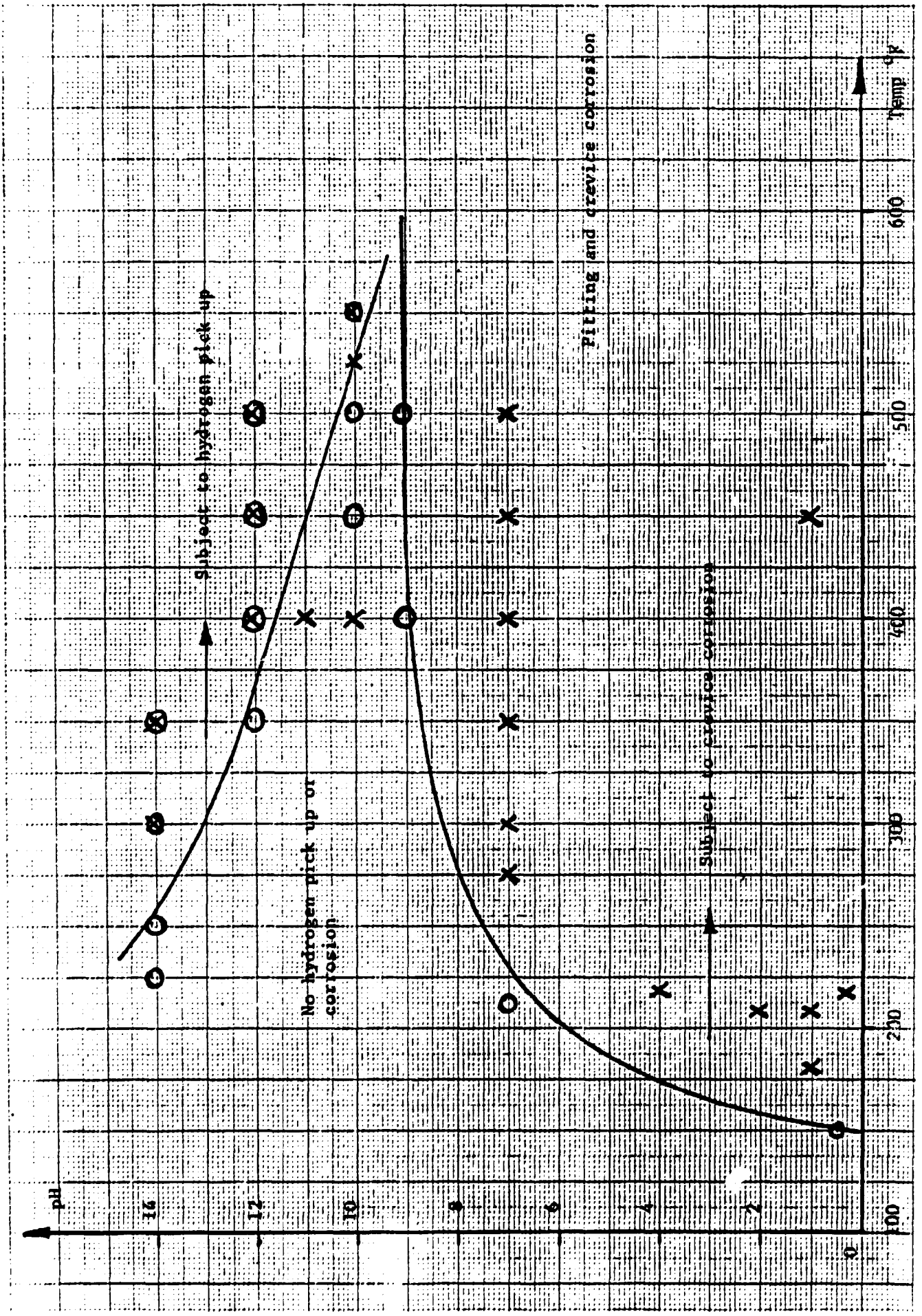


Fig. 10. Corrosion of Ti-Pd in Brine Solutions 24% NaCl (ref. 7)